

## Conversion of aluminum chlorohydrate to aluminum hydroxide

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### Synopsis

The structure of aluminum chlorohydrate, a highly soluble anti-perspirant, and aluminum hydroxide, an insoluble antacid, are discussed in relation to the mechanism of conversion of aluminum chlorohydrate to aluminum hydroxide. X-ray, IR, and  $^{27}\text{Al}$  NMR spectroscopic data indicate that aluminum chlorohydrate is composed of a central aluminum in tetrahedral configuration surrounded by 12 aluminums each in octahedral configuration. This highly charged complex is neutralized by 7 chloride counterions. In contrast, aluminum hydroxide has a polymer-like structure whose basic unit is a ring of six aluminums in octahedral configuration joined by double hydroxide bridges. Bayerite, an aluminum hydroxide polymorph, readily forms when the hydroxyl to aluminum ratio of aluminum chlorohydrate is raised to 3 by titration with sodium hydroxide. Dilution of aluminum chlorohydrate solutions with water or 0.9% NaCl leads to the formation of gibbsite, another aluminum hydroxide polymorph. Conversion of aluminum chlorohydrate occurs rapidly enough under simulated conditions of antiperspirant use to justify the conclusion that one mechanism of aluminum chlorohydrate's antiperspirant action is the formation of an obstructive aluminum hydroxide gel within the sweat duct.

### INTRODUCTION

The similarity between the empirical formulas for aluminum chlorohydrate,  $\text{Al}_2(\text{OH})_5\text{Cl} \cdot 2\text{H}_2\text{O}$  (1), and a type of aluminum hydroxide, which is used as an antacid,  $\text{Al}(\text{OH})_{2.55}\text{Cl}_{0.45}$  (2), suggests a relationship between these aluminum compounds. However, the extreme difference in aqueous solubility of these materials indicates different structural arrangements. A relationship between aluminum chlorohydrate and aluminum hydroxide is also suggested by recent studies on the mechanism of action of antiperspirants (3-6), which reveal an aluminum-containing plug in the duct of eccrine sweat glands following application of aluminum-containing antiperspirants. This observation supports the hypothesis that aluminum-containing antiperspirants act by forming an obstructive aluminum hydroxide gel within the sweat gland duct. It is thus important to examine the structure of aluminum chlorohydrate and aluminum hydroxide to determine if conversion is possible under the conditions encountered during the use of an antiperspirant.

## STRUCTURE OF ALUMINUM CHLOROHYDRATE

Figure 1 shows a characteristic X-ray diffractogram of aluminum chlorohydrate. The broad peak in the range of 4 to 10° 2θ shows a poorly ordered material with a d-spacing of 11.8 Å. The line broadening suggests a crystallite dimension of about 50 Å (7).

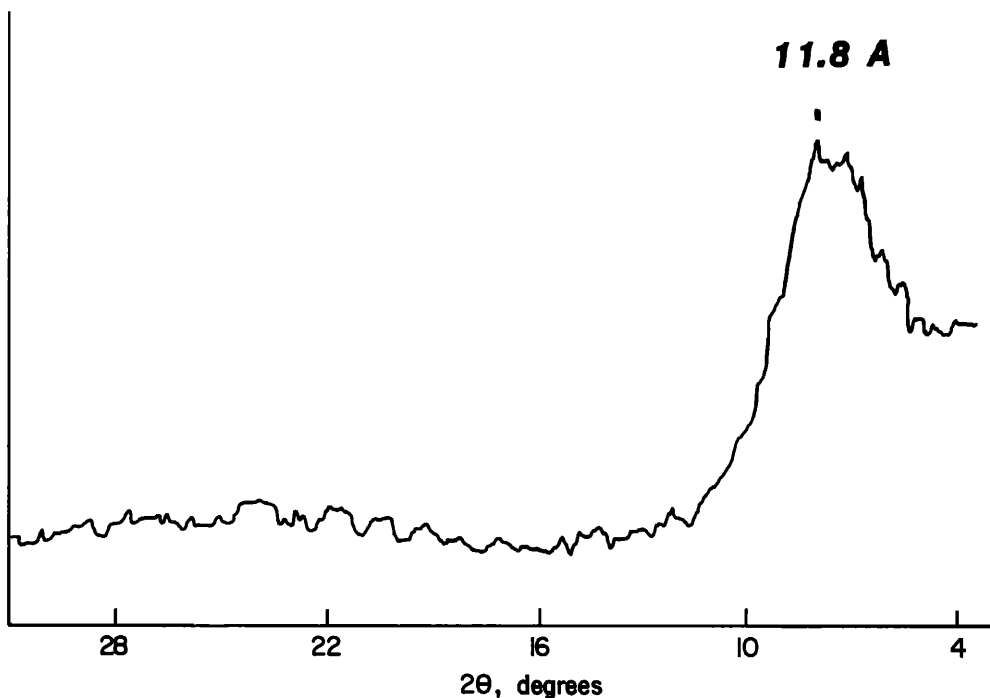
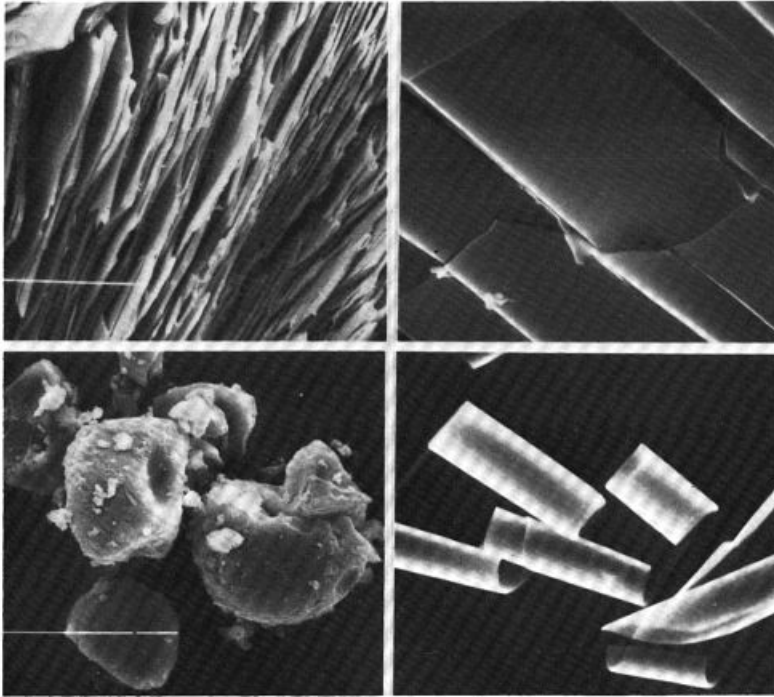


Figure 1. X-ray diffractogram of aluminum chlorohydrate. (Reproduced by permission from ref. 7.)

Further information on the molecular dimensions of aluminum chlorohydrate was obtained by observing that the interlayer spacing of montmorillonite increased by 8.9 Å as a result of intercalation of aluminum chlorohydrate (7).

Examination of the dimensions of highly hydrolyzed aluminum species reveal that the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex proposed by Johansson, *et al.*, (8) would be expected to cause the interlayer spacing of montmorillonite to increase by 9 Å following intercalation, as it is essentially a sphere of 9 Å diameter. The 9 Å dimension of the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex also agrees with the 11.8 Å d-spacing seen in the X-ray diffractogram (Figure 1) if a layer of water of hydration is associated with the aluminum chlorohydrate. The repeating unit of one  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex, 8.9 Å, and one water molecule, 2.9 Å, yields a d-spacing of 11.8 Å. The crystallite dimension of 50 Å suggests that the basic unit contains five aluminum chlorohydrate layers and their associated water layers.

The curling behavior of aluminum chlorohydrate seen by scanning electron microscopy following air drying (Figure 2) supports an alternating aluminum chlorohydrate and water arrangement; water will diffuse from between the aluminum chlorohydrate layers during air drying, resulting in a curled film (Figure 3).



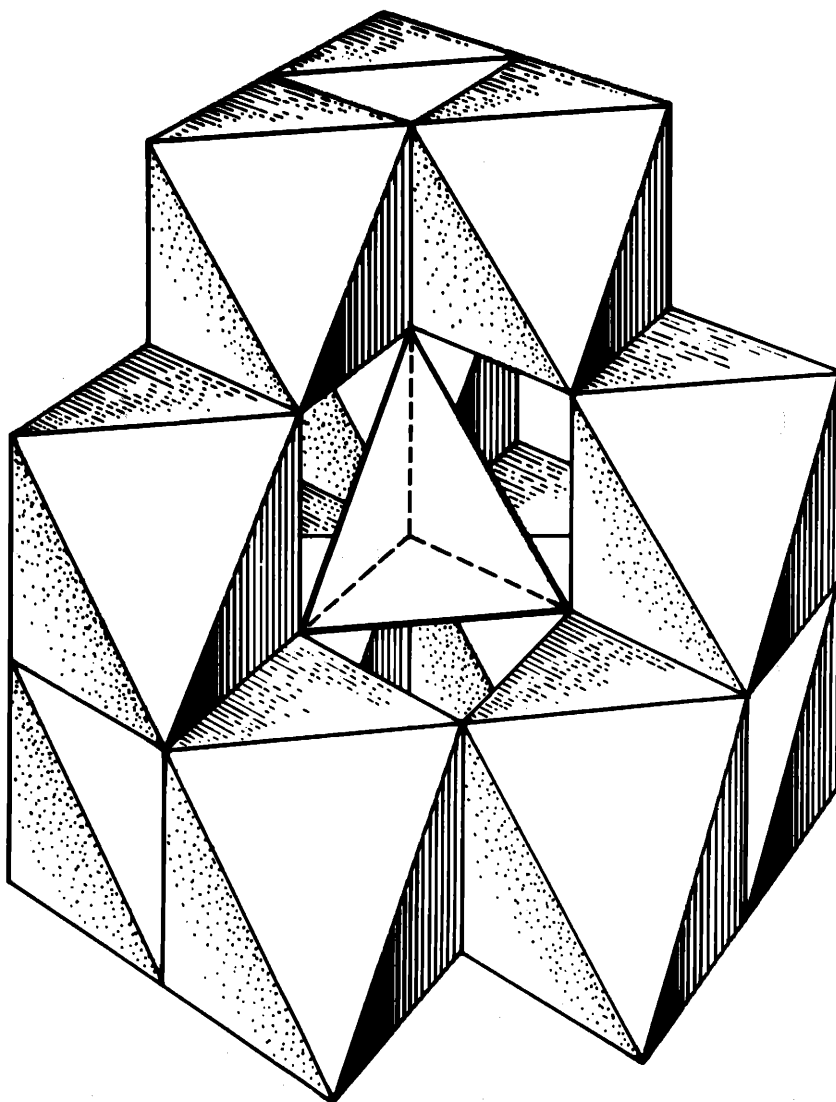
**Figure 2.** Scanning electron photomicrographs of aluminum chlorohydrate. Key: upper left, lyophilized, 700X, line of 50  $\mu\text{m}$ ; upper right, lyophilized, 5000X; lower left, spray dried, 2000X, line of 5  $\mu\text{m}$ ; and lower right, air dried 10,000X. (Reproduced by permission from ref. 9.)



**Figure 3.** Schematic effect of drying on material composed of alternating layers of aluminum chlorohydrate (ACH) and water.

**Table I**  
 Comparison of Empirical Formula for Aluminum Chlorohydrate,  $\text{Al}_2(\text{OH})_3\text{Cl} \cdot 2\text{H}_2\text{O}$ , and  
 $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}\text{Cl}_7$

	$\text{Al}_2(\text{OH})_3\text{Cl} \cdot 2\text{H}_2\text{O}$	$\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}\text{Cl}_7$
Al:Cl	2:1	13:7 (1.86:1)
Al:H <sub>2</sub> O	1:1	13:12 (1.08:1)
Al:OH	1:2.5	13:32 (1:2.46)



**Figure 4.** Structure of the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex showing the tetrahedral aluminum surrounded by 12 aluminums in octahedral configuration. (Reproduced by permission from R. Mesmer and C. Baes, *The Hydrolysis of Cations*, Wiley, New York, N. Y. 1976, Chap. 6.)

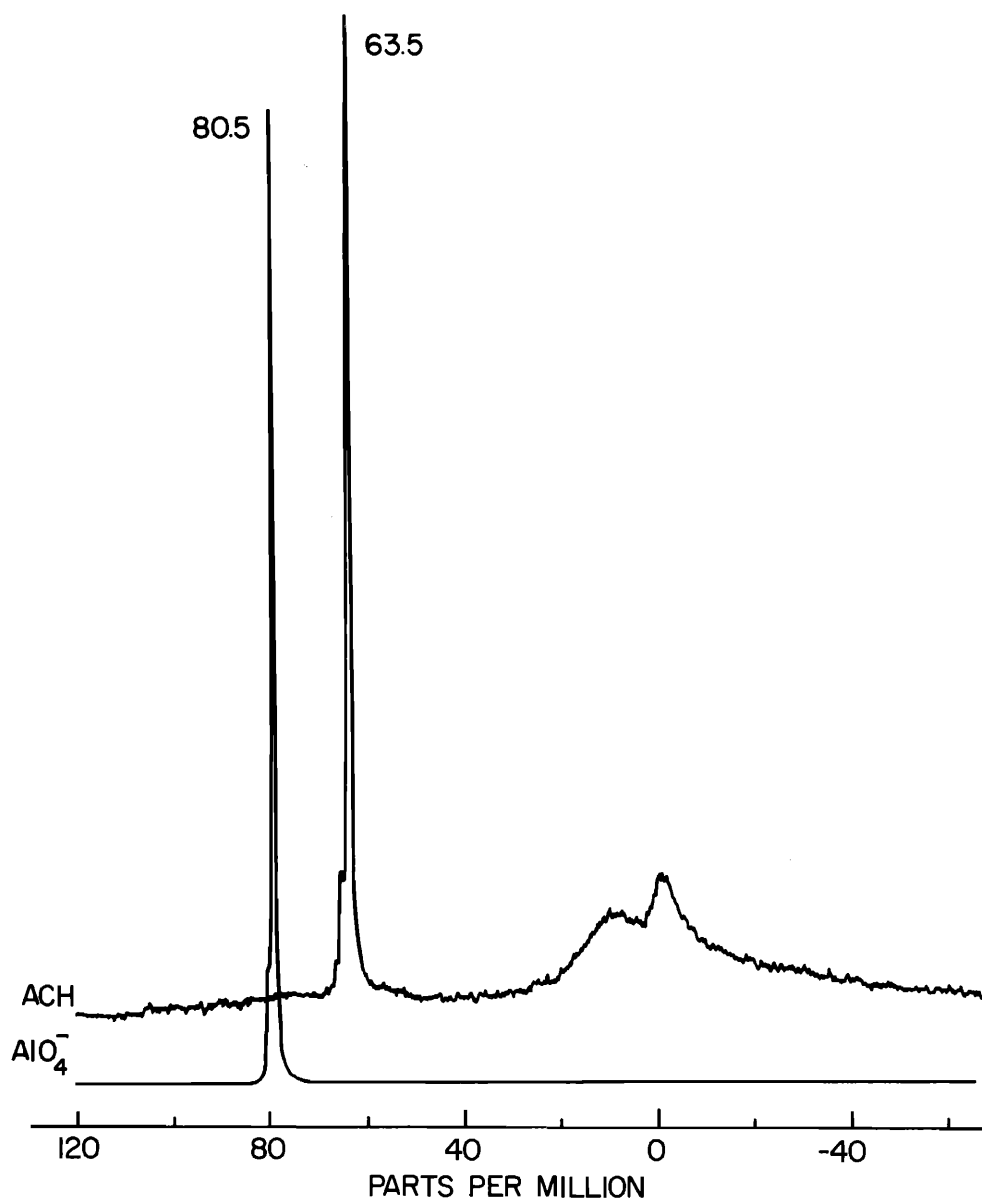
The empirical formula of aluminum chlorohydrate,  $\text{Al}_2(\text{OH})_3\text{Cl} \cdot 2 \text{H}_2\text{O}$  (1), compares favorably to the formula of the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex if seven chloride anions are assumed present to neutralize the charge of the complex and it is realized that the 4 oxygen atoms in the proposed complex will appear as 8 hydroxyl anions by the techniques used to establish the stoichiometry of aluminum compounds (Table I) (10). The small differences between the generally accepted empirical formula and the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex may be due to the presence of other aluminum species in aluminum chlorohydrate, and to the relatively nonspecific methods used for establishing the empirical formula.

The structure of the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex (Figure 4) is unusual because it contains a central aluminum in a tetrahedral environment surrounded by 12 aluminum atoms in octahedral environments. Aluminum in a tetrahedral environment is characterized by aluminate anion,  $\text{Al}(\text{OH})_4^-$ , which exists only at high pH conditions (11). Aluminum in octahedral configuration occurs at neutral and acidic pH, and is the configuration of aluminum in aluminum hydroxide (2). The presence of aluminum in both octahedral and tetrahedral environments can be determined by infrared and  $^{27}\text{Al}$  NMR spectroscopy.

The infrared spectrum of aluminum chlorohydrate shows a broad band between 3100 and 2500  $\text{cm}^{-1}$ , which represents the hydroxyl-stretching vibrations of aluminum in octahedral configuration (7). Infrared bands for aluminum in tetrahedral configuration occur at 345 ( $\text{AlO}_4$  antisymmetric bending), 640 ( $\text{AlO}_4$  symmetric stretching), and 780  $\text{cm}^{-1}$  ( $\text{AlO}_4$  antisymmetric stretching) (7). These bands agree closely with the infrared bands of sodium aluminate which occur at 325, 625, and 725  $\text{cm}^{-1}$  (12). The occurrence of the  $\text{AlO}_4$  symmetric- and antisymmetric-stretching frequencies at higher frequencies in aluminum chlorohydrate than in sodium aluminate indicates that a slightly longer Al-O bond is present in the tetrahedral aluminum of aluminum chlorohydrate. The Al-O bonds would be expected to be longer in a tetrahedral aluminum in which each oxygen was shared by an octahedral aluminum.

The  $^{27}\text{Al}$ -NMR spectrum of aluminum chlorohydrate at pH 4.8 has 3 distinct signals: a sharp peak at 63.5 ppm and two broad peaks at 1.7 and  $-0.4$  ppm (Figure 5) (7). The relative chemical shift differences were referenced to an external standard of  $\text{Al}(\text{H}_2\text{O})_6^{3+}$  at pH 1. For comparison, the  $^{27}\text{Al}$  NMR spectrum of sodium aluminate is also shown in Figure 5. The peak at 63.5 ppm indicates an Al-O bond in an  $\text{AlO}_4$  tetrahedral configuration. The peak width of less than 40 Hz suggests that the tetrahedral aluminum is not in equilibrium with the aqueous environment. Consequently, the tetrahedral  $\text{AlO}_4$  group is believed to be bonded to other aluminum atoms. The broad resonances at 1.7 and  $-0.4$  ppm suggest the presence of aluminum atoms in octahedral environments which are in rapid equilibrium with the aqueous solution.

The degree of interaction of the anion with the positively charged aluminum chlorohydrate complex could be studied by infrared spectroscopy if the anion were infrared active (13). Thus, aluminum chlorohydrate was treated with silver nitrate to replace the infrared-inactive chloride with nitrate. Nitrate was chosen because it is the same approximate size and charge as chloride, but it is also symmetrical so any perturbations in symmetry due to interaction with the aluminum complex will cause a shift in the infrared spectrum. The infrared spectrum of aluminum chlorohydrate was not affected by the replacement of chloride by nitrate except for the appearance of bands at 1380 and 830  $\text{cm}^{-1}$  (9). Both bands correspond to the 1358 and 836  $\text{cm}^{-1}$  bands



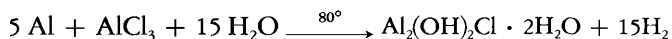
**Figure 5.**  $^{27}\text{Al}$ -NMR spectrum of aluminum chlorohydrate (ACH) and sodium aluminate ( $\text{AlO}_4^-$ ). (Reproduced by permission from ref. 7.)

for nitrate in sodium nitrate, indicating that the anion in aluminum chlorohydrate is readily exchangeable. The small shifts of the nitrate bands indicate a weak interaction of nitrate with aluminum chlorohydrate. Thus, the chloride anion is believed to function as a counterion in aluminum chlorohydrate.

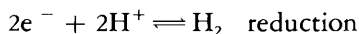
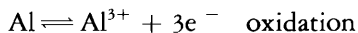
The evidence is strong that the basic unit of aluminum chlorohydrate consists of a central aluminum atom in tetrahedral environment which is surrounded by 12

aluminum atoms in octahedral environments. Tetrahedral aluminum is usually found only when the pH is above 10. However, the pH of aluminum chlorohydrate solutions is 4.5. The question arises as to how this symmetrical complex forms with a tetrahedral aluminum in the center.

The major synthetic procedure for preparing aluminum chlorohydrate involves the reaction of 5 moles of metallic aluminum with 1 mole of aluminum chloride (14).



The pH of the reaction begins near 3 and ends at approximately 4.5. Since the pH never rises above 4.5, it would be difficult for a tetrahedral aluminum to form in such a solution. However, regions of high pH may occur during the reaction even though the bulk solution is at a much lower pH. The main reactions which occur during the synthesis of aluminum chlorohydrate are the oxidation of metallic aluminum to aluminum ion and the reduction of protons to produce hydrogen gas.



These reactions occur only at the surface of the metallic aluminum. The protons arise from the dissociation of water. Since the protons are quickly converted to hydrogen gas, a high hydroxyl concentration may be present at the aluminum surface, resulting in the initial formation of aluminum atoms in tetrahedral configuration (Figure 6a). As a cluster of tetrahedral aluminum atoms diffuses away from the metallic aluminum surface (Figure 6b), the pH gradient causes the tetrahedral configuration to convert to the octahedral configuration. However, the tetrahedral aluminum in the middle of the cluster is protected from the acidic bulk solution, thus forming the  $\text{ Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex (Figure 6c). Seven chloride anions are associated with the complex as counterions.

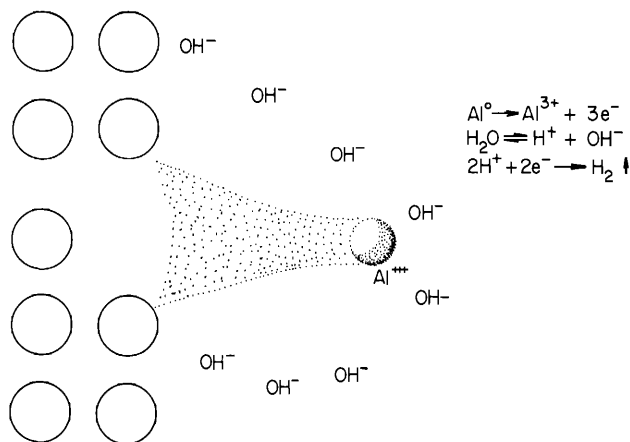


Figure 6a.

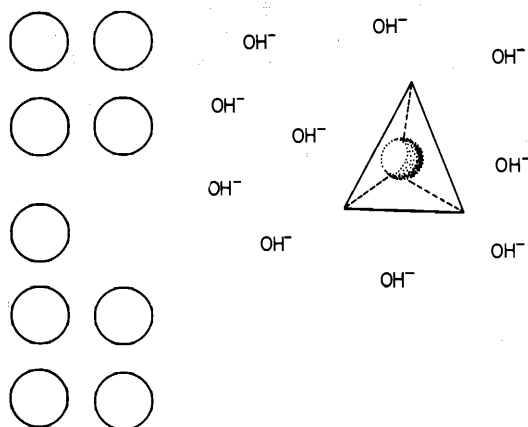


Figure 6b.

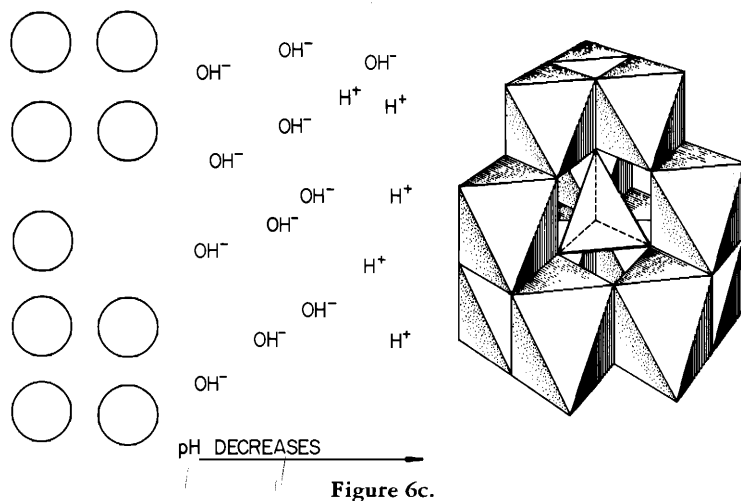


Figure 6c.

**Figure 6.** Schematic formation of aluminum chlorohydrate. Key: A, Release of aluminum cation from aluminum metal.; B, Formation of tetrahedral aluminum in region of high pH close to the aluminum metal surface.; C, Formation of  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex as tetrahedral aluminums diffuse away from aluminum metal surface and encounter a decreasing pH gradient.

### STRUCTURE OF ALUMINUM HYDROXIDE

Aluminum hydroxide may exist in the amorphous state as well as in several crystalline forms (15). Regardless of the polymorphic form, the aluminum atoms exist only in octahedral configuration. The aluminum octahedra may join at an edge to form a dimer by a deprotonation-dehydration reaction to join the two aluminum octahedra through a double hydroxide bridge (Figure 7). Two protons are released every time a



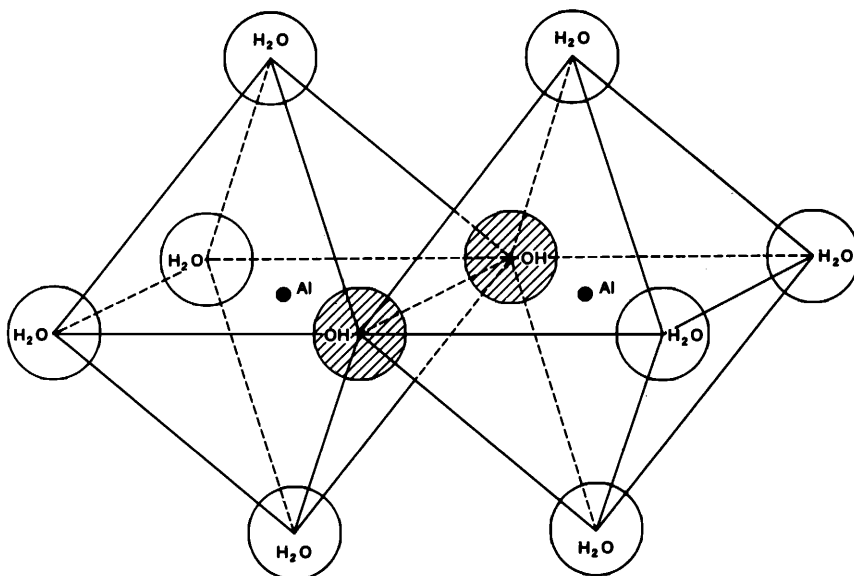


Figure 7. Dimeric cation  $\text{Al}_2(\text{OH})_2(\text{H}_2\text{O})_8^{4+}$ . (Reproduced by permission from ref. 16.)

double hydroxide bridge forms. The basic unit comprising aluminum hydroxide is a six member ring of aluminum octahedra joined by 6 double hydroxide bridges (16). Aluminum hydroxide in this state is amorphous and reacts rapidly with acid as all of the hydroxyls are accessible to protons. Crystallinity develops as the six member rings combine (Figure 8). This growth first occurs in one plane, but stacking gives rise to X-ray diffraction patterns which are identified as gibbsite, bayerite, norstrandite, or boehmite (15).

The development of order in aluminum hydroxide may be illustrated by infrared spectroscopy (17). Deuterium is heavier than hydrogen. Thus, O-D stretching occurs at a lower frequency than O-H stretching. When a freshly precipitated aluminum hydroxide gel is air dried and exposed to  $\text{D}_2\text{O}$  vapor, all of the hydroxyls are converted to deuterioxylys, indicating that all of the hydroxyls are accessible for exchange (Figure 9a). As the aluminum hydroxide gel ages, the hydroxyls incorporated into ordered or crystalline phases become unavailable for exchange with  $\text{D}_2\text{O}$  (Figure 9b). The hydroxyls which are not accessible for exchange begin to show the characteristic infrared spectrum of gibbsite (Figure 9f). Thus it is clear that aluminum hydroxide is composed exclusively of aluminum in octahedral configuration and that the basic unit is a six member ring of octahedral aluminum joined by double hydroxide bridges.

#### STRUCTURAL CHANGES IN ALUMINUM CHLOROHYDRATE FOLLOWING ADDITION OF BASE

The addition of sufficient sodium hydroxide to aluminum chlorohydrate to bring the hydroxyl to aluminum ratio from 2.5 to 3.0 initiated structural changes which were

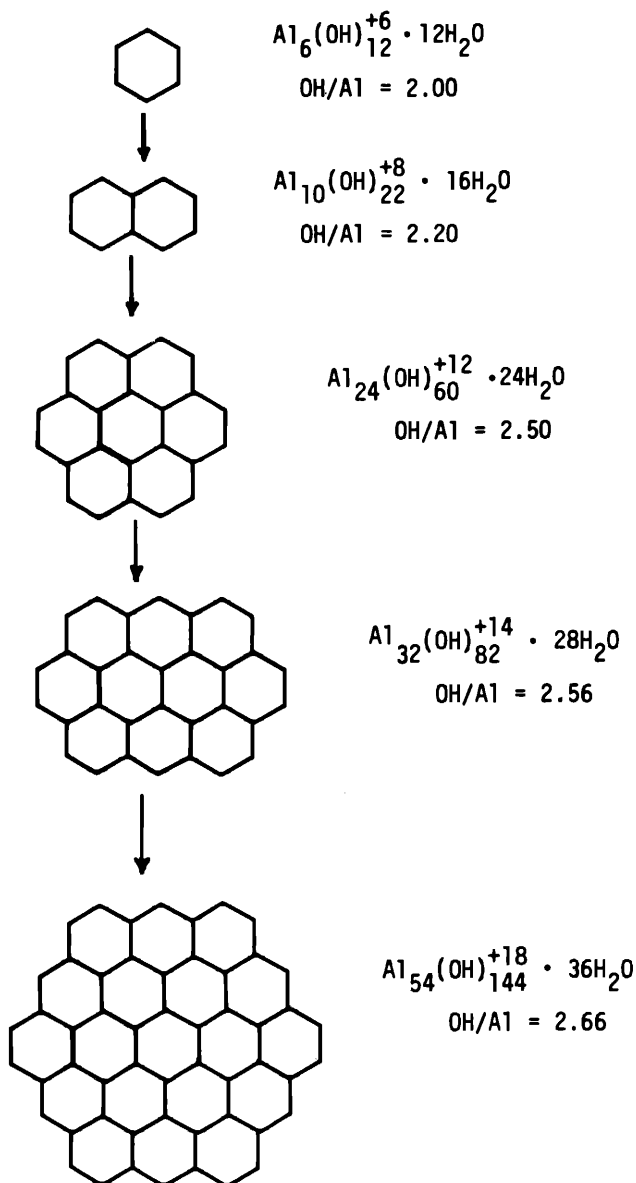
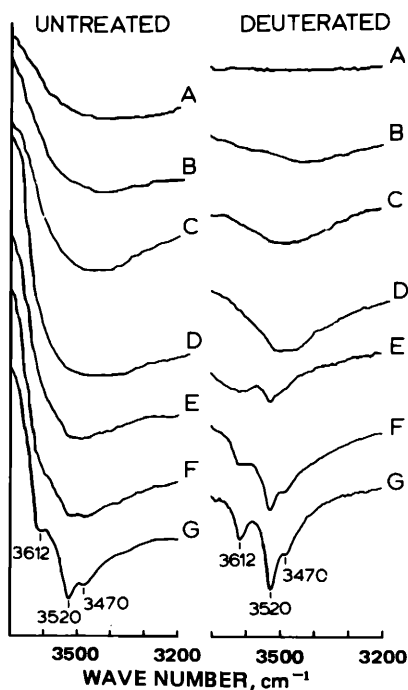


Figure 8. Development of crystalline aluminum hydroxide. (Reproduced by permission from ref. 2.)

monitored by infrared spectroscopy (Figure 10). Indications of distinct absorption bands in the hydroxyl-stretching region were seen after aging for 10 days at 25°. Sharp hydroxyl-stretching bands at 3650, 3540, and 3460  $\text{cm}^{-1}$  were apparent after 111 days, which correspond to the hydroxyl-stretching vibrations of bayerite (11). The X-ray diffractogram after 111 days confirms that the aluminum chlorohydrate converted to bayerite after the addition of base (Table II). Bayerite is the aluminum hydroxide polymorph which forms under basic conditions (15).

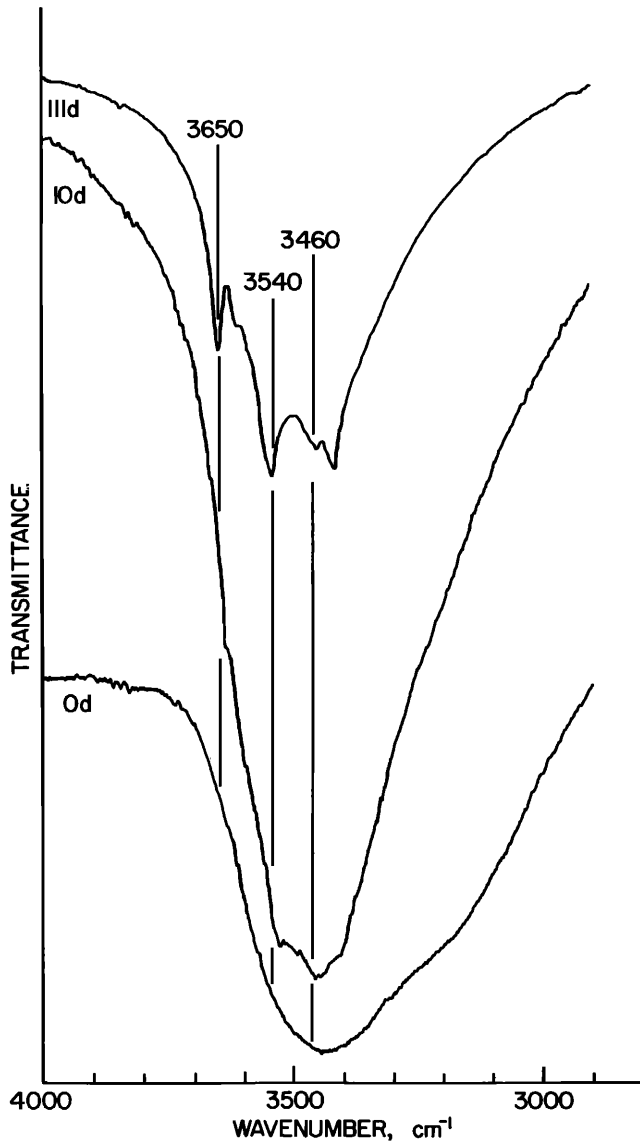


**Figure 9.** Change in hydroxyl-stretching frequency region of IR spectrum of aluminum hydroxide gel for untreated and deuterated samples during aging at 25°. Key: A, fresh precipitate; B, 42 days; C, 59 days; D, 74 days; E, 81 days; F, 97 days; and G, 147 days. (Reproduced by permission from ref. 17.)

### STRUCTURAL CHANGES IN ALUMINUM CHLOROHYDRATE FOLLOWING DILUTION

Aluminum chlorohydrate is also unstable upon dilution with water. When a commercial aluminum chlorohydrate solution (6.2 M in aluminum) was diluted to  $2.5 \times 10^{-2}$  M in aluminum, the pH increased initially but later decreased (Figure 11). The diluted aluminum chlorohydrate solution became turbid after 3 days, corresponding to the time when the pH began to decrease. The insoluble phase was collected by filtration and examined by infrared spectroscopy (Figure 12). The hydroxyl-stretching bands of the insoluble phase coincide with the hydroxyl-stretching bands of gibbsite, the polymorph of aluminum hydroxide which forms under acidic conditions (15). The infrared spectrum of the lyophilized filtrate was identical to the reference spectrum of aluminum chlorohydrate.

It is believed that dilution of aluminum chlorohydrate causes the highly charged aluminum polycations to become widely separated, thereby reducing the stabilizing effect of the chloride counterions and the other aluminum chlorohydrate complexes. The tetrahedral aluminum is exposed to the aqueous environment as the  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  complex dissociates. Since the octahedral configuration is the stable form of aluminum in acidic solution, the tetrahedral aluminum converts to an octahedral configuration. Exposure of the four negatively charged oxygens, which form the outer shell of the aluminum tetrahedron, to the aqueous environment results in the attraction of protons and water to complete the octahedral configuration. The adsorption of protons is reflected in the initial increase in pH. However, the long term



**Figure 10.** Change in hydroxyl-stretching frequency region of IR spectrum following neutralization of aluminum chlorohydrate. Key: bottom curve, initial; middle curve, after 10 days at 25°; and top curve, after 111 days at 25°. (Reproduced by permission from ref. 18.)

**Table II**  
X-ray Diffractogram of Aluminum Chlorohydrate Before and After Neutralization

Interplanar Spacing, Å		
Before Neutralization	111 Days After Neutralization	Bayerite
11.8	4.72	4.72
	4.35	4.36
	3.20	3.19
	2.22	2.21
	1.72	1.71

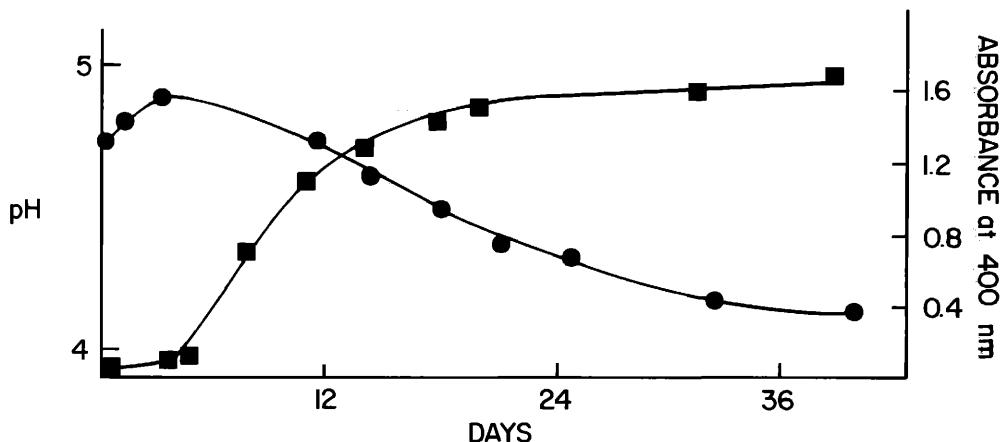


Figure 11. Change in pH (●) and turbidity (■) following dilution of aluminum chlorohydrate to  $2.5 \times 10^{-2}$  M in aluminum during aging at  $25^\circ$ . (Reproduced by permission from ref. 18.)

pH trend is downward, which is consistent with the polymerization of octahedral aluminum by the deprotonation-dehydroxylation mechanism.

#### CONVERSION OF ALUMINUM CHLOROHYDRATE TO ALUMINUM HYDROXIDE UNDER SIMULATED CONDITIONS OF ANTIPERSPIRANT USE

The conversion of aluminum chlorohydrate to aluminum hydroxide by addition of base or dilution requires several days. However, when aluminum chlorohydrate is used as an antiperspirant, it is simultaneously diluted with sweat and exposed to a higher pH at body temperature. Thus, it is important to determine if conversion of aluminum chlorohydrate to aluminum hydroxide can occur rapidly enough under simulated conditions of use to justify the conclusion that aluminum chlorohydrate acts as an antiperspirant by the formation of an obstructive aluminum hydroxide gel within the sweat gland duct. As seen in Table III, an insoluble phase formed immediately when the pH of commercial aluminum chlorohydrate (6.2 M in aluminum) was adjusted to pH 5 or above. Upon tenfold dilution with 0.9% NaCl, a solid phase still formed immediately when the pH was raised to 5 or above. A solid phase appeared within 24 hours at pH 6 following 100 fold dilution with 0.9% NaCl, and in 2 hours at pH 7 following 1000 fold dilution with 0.9% NaCl. Thus, the combination of elevated pH and dilution with 0.9% NaCl at  $37^\circ$  leads to the rapid conversion of aluminum chlorohydrate to aluminum hydroxide, and supports the mechanism of antiperspirant action which is based on a plug of aluminum hydroxide forming in the eccrine sweat duct.

The conversion of aluminum chlorohydrate to aluminum hydroxide is expected once the structures of both compounds are understood. Disintegration of aluminum chlorohydrate releases 12 octahedral aluminum atoms and 1 tetrahedral aluminum atom. When the tetrahedral aluminum is exposed to the aqueous environment of the sweat duct, it converts to an octahedral configuration. The octahedral aluminum atoms readily organize into aluminum hydroxide by the dehydration-deprotonation mechanism.

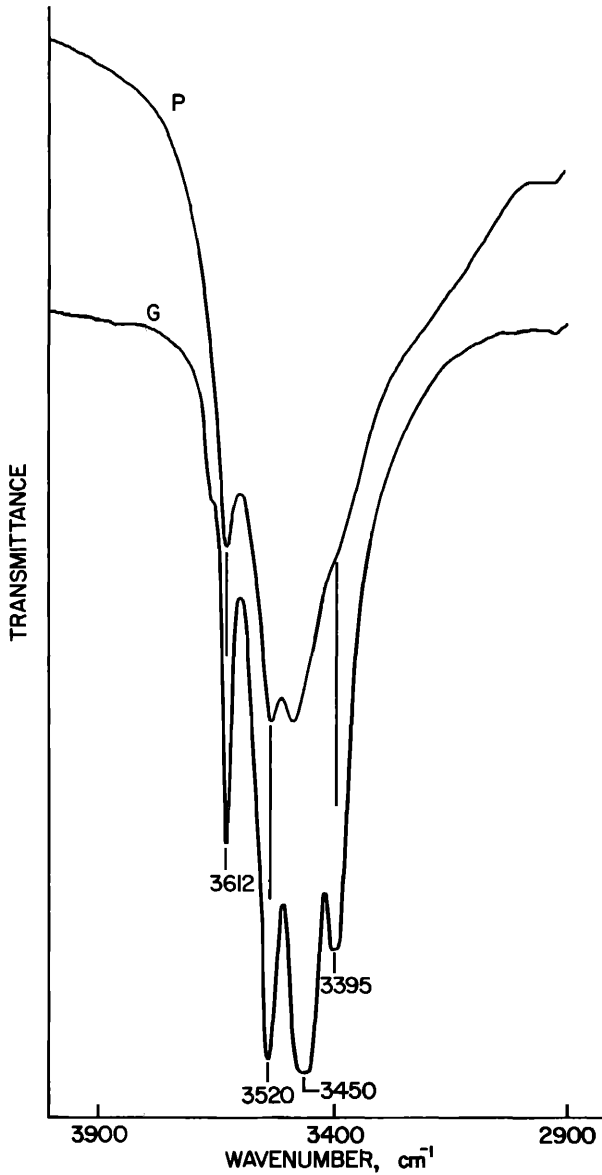


Figure 12. Hydroxyl-stretching frequency region of IR spectrum of solid dilution of aluminum chlorohydrate to  $2.5 \times 10^{-2}$  M in aluminum (P) compared to natural gibbsite (G). (Reproduced by permission from ref. 18).

**Table III**  
Time for Precipitate to Appear at 37° Following Dilution with 0.9% NaCl and pH Adjustment

ACH, M	pH				
	5.0	5.5	6.0	6.5	7.0
6.2	I	I	I	I	I
0.62	I	I	I	I	I
0.062	C	C	24 hr	I	I
0.0062	C	C	C	C	2 hr

I = Immediate Precipitate  
C = Clear for 3 days

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